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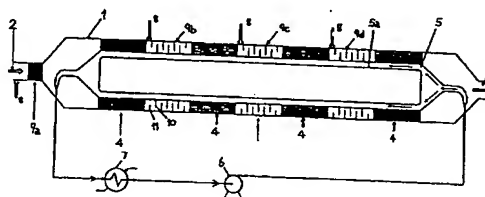
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(54) CUVE DE REACTION ET PROCEDE PERMETTANT D'ELIMINER LE MONOXYDE DE CARBONE DANS
L'HYDROGENE

(54) REACTOR AND PROCESS FOR REMOVAL OF CARBON MONOXIDE FROM HYDROGEN

(57)

²²²A reactor vessel (1) contains one or more selective oxidation stages and has ²counter-current cooling (5, 6, 7), each stage having an inlet for feedstock ²such as CO-contaminated hydrogen (2), an inlet for a second feedstock such as ²oxygen or air (8), gas mixing means (9a, 9b) and a catalytic reaction zone ²(4), preferably containing a metal support carrying a selective oxidation ²catalyst. A compact reformer with a very low pressure drop is suitable for ²producing hydrogen for fuel cell.²



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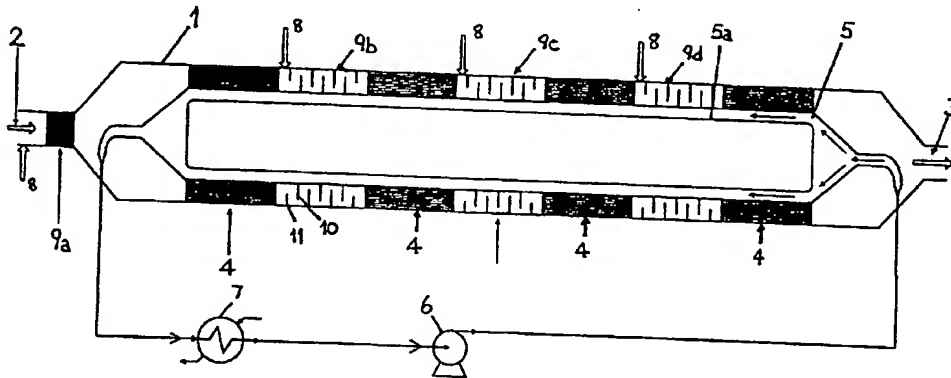
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(57) Abrégé/Abstract

A reactor vessel (1) contains one or more selective oxidation stages and has counter-current cooling (5, 6, 7), each stage having an inlet for feedstock such as CO-contaminated hydrogen (2), an inlet for a second feedstock such as oxygen or air (8), gas mixing means (9a, 9b) and a catalytic reaction zone (4), preferably containing a metal support carrying a selective oxidation catalyst. A compact reformer with a very low pressure drop is suitable for producing hydrogen for fuel cell.

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| (54) Title: REACTOR AND PROCESS FOR REMOVAL OF CARBON MONOXIDE FROM HYDROGEN (57) Abstract <p>A reactor vessel (1) contains one or more selective oxidation stages and has counter-current cooling (5, 6, 7), each stage having an inlet for feedstock such as CO-contaminated hydrogen (2), an inlet for a second feedstock such as oxygen or air (8), gas mixing means (9a, 9b) and a catalytic reaction zone (4), preferably containing a metal support carrying a selective oxidation catalyst. A compact reformer with a very low pressure drop is suitable for producing hydrogen for fuel cell.</p> | | |

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REACTOR AND PROCESS FOR REMOVAL OF CARBON MONOXIDE FROM HYDROGEN

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The present invention concerns an improved reactor, more particularly it concerns a reactor particularly adapted for and suitable for certain selective oxidation reactions.

We have previously developed certain selective oxidation processes for the removal of residual carbon monoxide in hydrogen-containing gases intended as feedstock for fuel cells. Such processes are disclosed and claimed in for example, PCT/GB98/02873. It has become well established that hydrogen-fuelled fuel cells require very low proportions of carbon monoxide, which acts as a catalyst poison and degrades performance of the fuel cell. Desirably, the amount of CO is less than 10 ppm. If a liquid fuel is reformed to form a hydrogen-containing fuel, levels of CO are produced which may vary about 0.5-5mol%, so that it becomes necessary to attenuate such CO levels. As mentioned in the above International Application, catalytic selective oxidation reactions are highly exothermic with the result that increasing reaction temperatures lead to increasing loss of valuable hydrogen due to competing reactions.

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There remains a need for a catalytic selective oxidation reactor which permits good temperature control yet is simple, effective and inexpensive to manufacture. Although hydrogen "cleaned-up" by the reactor of the present invention may be used as fuel cell fuel, there are many other uses for such hydrogen. Also, although the reactor is particularly suitable for the cleaning up of reformat (which may be from methanol, other oxygenated fuels, gasoline or other hydrocarbon fuels), it is not limited to such use. Accordingly, the present invention provides a reactor for catalytic selective oxidation, comprising a reactor vessel with counter current cooling and at least one stage, each stage provided with an inlet for a first feedstock, e.g. CO contaminated hydrogen, an inlet for a second feedstock, e.g. oxygen-containing gas, gas mixing means and a catalytic reaction zone, preferably comprising a selective oxidation catalyst deposited on a substrate having good heat conduction properties.

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The invention also provides a process for the removal of quantities of CO from a hydrogen feedstock by partial oxidation, comprising at least one step of admixing said

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feedstock with a quantity of oxygen, passing the resulting mixture over a selective oxidation catalyst in a selective oxidation zone and recovering a hydrogen product with reduced content of CO, whilst simultaneously cooling the selective oxidation zone, preferably to maintain the selective oxidation zone at a temperature in the range 100 to 250°C, by counter-current coolant flow.

The reactor, in its most preferred embodiment, has four stages and this is effective to reduce a reformat having a CO content of 1 to 2% to below 10ppm. In other embodiments, there may be 2 to 10 stages.

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The reactor is suitably in the form of a vessel in which the reaction zones are generally annular in shape, and provided with internal and/or external liquid cooling. Cooling is preferably provided by internal cooling using water, which is suitably under pressure to prevent boiling at the temperatures generated. Other liquid coolants, or forced air cooling may be used if desired. According to specific reactor designs, heat removal may be enhanced by increasing heat exchange surface areas by corrugation or other established means. Heat removal may be altered by altering the flow of coolant and/or altering the quantity of heat removed from the coolant by means of a heat exchanger.

Each reaction zone suitably comprises a metallic catalyst support ("monolith") of generally honeycomb construction, as is in common use in automobile exhaust gas catalysis. These may have 50 to 1200 cells per square in cell density, preferably 200 to 600 cpsi, and may be of a variety of types of stainless steel. In general, the present invention does not result in the reaction stages reaching the higher temperatures generally met with in exhaust gas catalysis (e.g. 500-900°C), but the material should be capable of resisting temperature excursions. An alternative reaction zone design utilises what has become known as "static mixers" which combine a very high degree of gas agitation and mixing, resulting in non-laminar flow, with relatively low pressure drop. Such static mixers may be manufactured from a variety of metals and are commercially available. However, it is presently preferred to use a honeycomb monolith.

The reaction zone desirably carries a selective oxidation catalyst comprising a platinum group metal, especially comprising platinum and/or rhodium, carried on a high

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surface area metal oxide support, such as alumina. The metallic catalyst support may be coated by generally known methods with a slurry of oxide support, dried and fired, and then impregnated with the catalytically active components, before a final firing. Such procedures are in themselves known, and do not form part of this invention.

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The invention will now be described with reference to the accompanying drawing which shows a cross-section of one embodiment of the present invention.

An essentially cylindrical metal vessel, made by pressing two halves and seam-welding, has a main gas inlet, 2, for reformat gas, and an outlet, 3, for cleaned gas. The vessel has a number of annular reaction zones, 4, each consisting of an annular wound corrugated catalyst support. The vessel further has an internal water jacket, 5, between a spacer and the shell and this is supplied with cooling water by means of a water circuit comprising a circulating pump, 6, and a heat exchanger, 7. The heat exchanger is desirably used to recover heat in an integrated system e.g. in an integrated combined heat and power system. The vessel further is provided with four air inlets, 8, each providing pre-determined (for a steady-state operation) levels of air (that is reaction oxygen; air is generally suitable). Although not preferred, controlled amounts of oxygen, according to one or more feedback or feed forward controls detecting gas flow levels and CO levels may be used. Downstream of each air inlet is a gas mixing zone, 9a, 9b, 9c and 9d. Zone 9a is suitably a static mixer, but zones 9b, 9c and 9d are preferably alternating annular mixing vanes, 10, and discs, 11, having gas flow holes, as illustrated in Figs 2 and 3. It should be noted that for simplicity only four vanes and four holes are shown, but more, e.g. six or eight, may be used. Such vanes and discs may be manufactured by pressing to form a sleeve which may be fitted and brazed or welded onto the jacket 5 with the intention that each gas mixing zone also serves to remove heat from the reaction gases leaving each reaction zone. Although the schematic drawing of the reactor shows each reaction zone and gas mixing zone of the same size, these may be designed to differ according to the amount of heat to be removed. Additionally, each reaction zone may incorporate different and/or different loadings, of catalyst. Each metal catalyst support monolith suitably has 300-400 cells per sq.in. and is coated with a washcoat comprising ~36wt% alumina solids of D50 of approx 5µm and D90 of approx 16µm, to deposit approx 3g/m³. After drying and firing, the coated monolith was impregnated with

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a platinum salt solution to result in 5% by wt of Pt deposited on the alumina. The resulting coated monolith was again dried and fired before being assembled into the reactor.

Initial studies indicate that a reformat containing 1-2% CO in admixture with H₂, CO₂, N₂, water vapour with a small proportion of unreacted reformer feedstock (e.g. CH₃OH, CH₄, gasoline), at 180°C may be converted to a feed gas suitable for a fuel cell, containing below 10ppm CO, and at 140°C.

The reactor of the invention is compact and exhibits relatively low pressure drop. Manufacturing costs are relatively low. The reactor is believed to be suitable for mobile or automobile uses as well as stationery uses. It is presently envisaged that the reactor shell will be lagged to control heat loss and prevent injury. The reactor can be manufactured simply and inexpensively, using pressed and welded parts. It is desirably operated to achieve low pressure drop, and the particular embodiment illustrated is designed for a gas hourly space velocity of approx. 30,000h⁻¹ gas throughput.

The reactor as described may be altered in a variety of ways without departing from the central inventive concept.

The invention is now illustrated below in a working example of a two-stage reactor, fed with a synthetic reformat gas mixture containing N₂, H₂, CO, CO₂ and H₂O. Each of the two stages consists of a mixing zone with three off-set spiral vanes, followed by air injection accomplished through a number of apertures in an annular ring, producing a swirling, mixing gas. The thus mixed hydrogen and air mixture passes through an annular metal honeycomb support mounted on a central cooling jacket. The cooling jacket is fed counter-current to the flow of hydrogen with a heat transfer fluid, conveniently water under pressure, and the metal honeycomb support is mounted in good heat exchange contact with the cooling jacket. The metal honeycomb carries a selective oxidation catalyst. Gas may be extracted for analysis between the two stages and/or after the second stage. By setting the composition of the feedstock gas mixture according to that analysed after the first or second stage, the test two-stage reactor can model a three or four stage reactor.

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The detailed operating conditions and other experimental detail for one typical run of the above reactor now follow. It was remarkable that the pressure drop across the whole of the est reactor was about the measurement limit of the gauges being used, and was of the order of 1.5-3mbar (150-300Pa), at the two throughputs tested. This indicates that the reactor is very efficient, compact and requires very little energy to operate.

1. Each catalyst support was an annular of internal diameter 3.85in (9.78cm), external diameter 5.85in (14.86cm) and 3.0in(7.62cm) length, made from "Fecralloy" steel and having 500 cells per sq in. Each support had been washcoated with alumina washcoat as used in exhaust gas catalytic convertors, followed by loading with 5% by wt of the alumina of Pt. Conventional manufacturing techniques were used.
2. The synthetic reformat had the compositions: 48%N₂(dry), 40%H₂ (dry), 10%CO₂(dry), 0.5-1.5%CO (dry) and 13% H₂O (of total flow). Two levels of CO concentration were chosen, a higher level to represent the output from autothermal reforming, and a lower level to represent the output from steam reformer or an optimised reformer, and two levels of throughput stated to be Nominal 3kWe (1kilowatt equivalent = 1,000 l/hr of H₂) and Nominal 6kWe, equal to 7,5000 l/hr of dry reformat and 15,000 l/hr of dry reformat respectively (8,620 l/hr and 17,240 l/hr of wet reformat).

It is plain from these results with a two-stage reformer that the compact and efficient reformer of the invention will be effective to remove CO from Hydrogen to any desired level, by conventional optimisation and especially by matching the number of stages to the requirements of the fuel cell system or other usage of the purified hydrogen.

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TWO-STAGE ANNULAR SELOX REACTOR TEST RESULTS

| SECOND STAGE | | | | | | | | | | | |
|--------------|--------------------------|-----------------|----------------|--------------|----------------|------------------|----------------|---------------|----------------|-------------------|-------|
| FIRST STAGE | | | | | | | | | | | |
| Ex No. | Power kW _e | CO in %, dry | Air in, slm | Temp in C | Temp out, C | CO out %, dry | Air in, slm | Temp in, C | Temp out, C | CO out ppm dry | Sel** |
| 1 | 3 | 1.5 | 4 | 125 | 212 | 0.60 | 2 | 167 | 212 | 1610 | 0.696 |
| 2 | 3 | 1.5 | 4 | 127 | 214 | 0.60 | 3 | 167 | 217 | 740 | 0.640 |
| 3 | 3 | 1.5 | 4 | 125 | 210 | 0.60 | 4 | 169 | 227 | 950 | 0.556 |
| 4 | 3 | 1.5 | 3 | 125 | 149 | 0.81 | 3 | 129 | 175 | 1840 | 0.684 |
| 5 | 3 | 1.5 | 5 | 128 | 215 | 0.34 | 3 | 161 | 220 | 290 | 0.582 |
| 6 | 3 | 0.5 | 2 | 143 | 176 | 0.122 | 0.5 | 138 | 145 | 232 | 0.579 |
| 7 | 3 | 0.5 | 2 | 141 | 167 | 0.122 | 0.8 | 127 | 136 | 29 | 0.540 |
| 8 | 3 | 0.5 | 2 | 140 | 161 | 0.122 | 1.0 | 121 | 130 | 28 | 0.505 |
| 9 | 3 | 0.5 | 2 | 141 | 172 | 0.122 | 1.2 | 131 | 146 | 55 | 0.472 |
| 10 | 3 | 0.5 | 1.5 | 142 | 166 | ? | 1.0 | 134 | 157 | 373 | 0.562 |
| 11 | 3 | 0.5 | 2.5 | 142 | 179 | ? | 1.0 | 138 | 150 | 50 | 0.433 |
| 12 | 6 | 0.5 | 4 | 138 | 167 | 0.130 | 1 | 148 | 176 | 722 | 0.520 |
| 13 | 6 | 0.5 | 4 | 138 | 162 | 0.130 | 2 | 140 | 185 | 51 | 0.503 |
| 14 | 6 | 0.5 | 4 | 138 | 166 | 0.130 | 3 | 146 | 198 | 105 | 0.428 |
| 15 | 6 | 0.5 | 6 | 138 | 205 | 62ppm | 0 | 176 | 174 | 62 | 0.502 |

** Sel: (Selectivity) = CO consumed/2 x O₂ consumed

CLAIMS

1. A catalytic selective oxidation reactor, comprising a cylindrical reactor vessel (1) with counter current cooling means (5,6,7) and at least one stage, each stage being
5 provided with an inlet for a first feedstock (2), and inlet for a second feedstock (8), gas mixing means (9) and a catalytic reaction zone (4), wherein the reaction zone comprises a selective oxidation catalyst deposited upon a metal support.
2. A reactor according to claim 1, wherein the metal support is mounted in good heat
10 exchange contact with the cooling means.
3. A reactor according to any one of the preceding claims, wherein the metal support is a metal monolith.
- 15 4. A reactor according to any one of the preceding claims, wherein the cooling means comprises a central jacket mounted within the reactor.
5. A reactor according to claim 4, wherein the central jacket is connected via a coolant circuit to an external heat exchanger.
- 20 6. A reactor according to claim 4 or 5, wherein the central jacket is connected via a coolant circuit to a circulating pump.
7. A reactor according to any one of the preceding claims, wherein the catalytic reaction
25 zone(s) is/are annular and surround a central cooling means.
8. A reactor according to any one of the preceding claims, having from 2 to 10 stages.
9. A reactor according to claim 8, having four stages.
- 30 10. A reactor according to any one of the preceding claims, wherein the gas mixing means comprise annular mixing vanes or discs.

AMENDED SHEET

11. A reactor according to any one of the preceding claims, connected to the output from a reformer such that CO is removed from the output gas to a level where the output from the reactor may be fed to a fuel cell.
- 5 12. A process for the removal of quantities of CO from a hydrogen feedstock by partial oxidation, comprising at least one step of admixing said feedstock with a quantity of oxygen, passing the resulting mixture over a selective oxidation zone comprising a selective oxidation catalyst on an annular metal support, and recovering a hydrogen product with reduced content of CO, whilst simultaneously cooling the selective
10 oxidation zone by counter-current coolant flow.
13. A process according to claim 12, wherein the selective oxidation zone is maintained at a temperature in the range 100 to 250°C.
- 15 14. A process according to claim 12 or 13, providing hydrogen to a fuel cell.

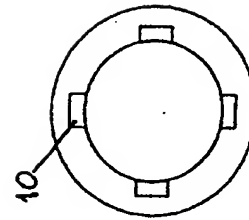
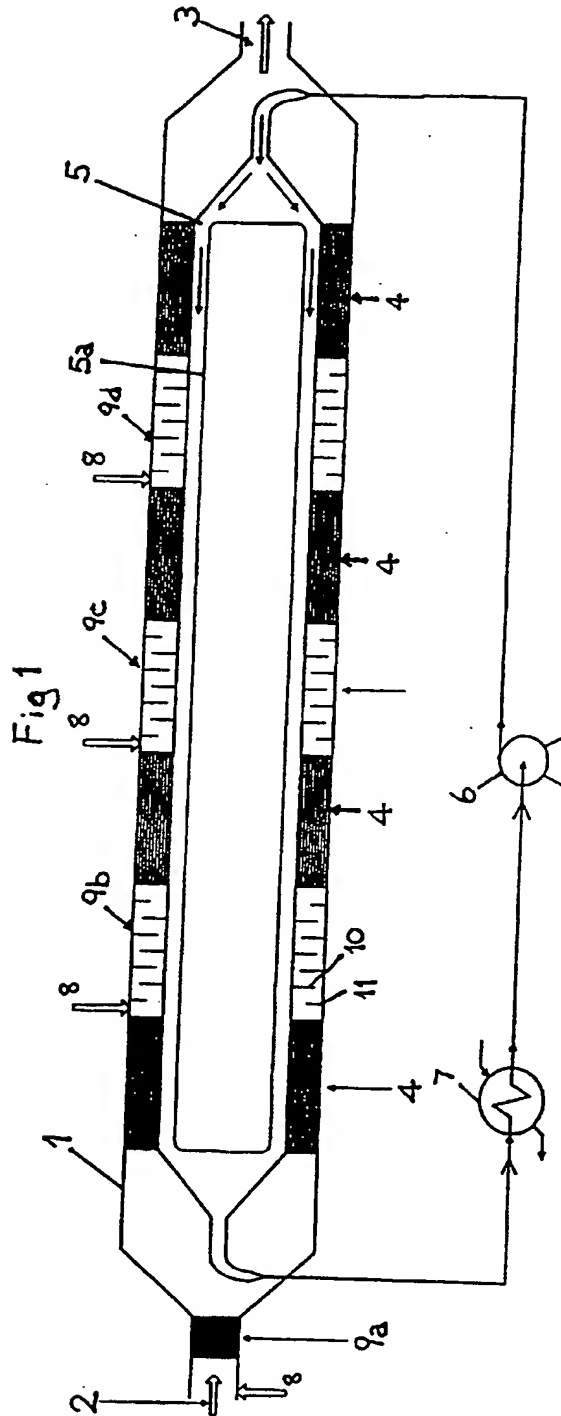


Fig 3

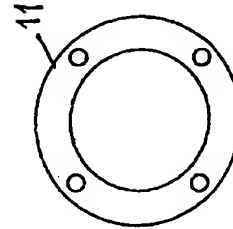


Fig 2